

SULFUR HEXAFLUORIDE AT CAPE GRIM: LONG TERM TRENDS AND REGIONAL EMISSIONS

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Abstract

Sulfur hexafluoride (SF₆) has been measured at Cape Grim since 1978 via a combination of *in situ* and flask measurements, including measurements on the Cape Grim air archive. The long-term growth rate of SF₆ as observed at Cape Grim has increased from 0.1 ppt yr⁻¹ in the late 1970s to 0.24 ppt yr⁻¹ in the mid-1990s. Since then the growth rate has remained relatively constant at 0.23±0.02 ppt yr⁻¹, indicating relatively constant global emissions (±10 %) since 1995. Pollution episodes at Cape Grim have been used to estimate regional (Melbourne and environs) and Australian emissions of SF₆ at 3±1.5 and 15±7.5 tonnes yr⁻¹ during 2001-2003.

1. Introduction

Sulfur hexafluoride (SF₆) is a very long-lived trace gas with an atmospheric lifetime in excess of 3,000 years and a Global Warming Potential (GWP) in excess of 15,000 [Montzka and Fraser, 2003]. Sulfur hexafluoride, which is used mainly in high voltage electrical switching equipment, was first identified in the atmosphere in 1970 at background levels of 0.03 ppt [parts per trillion (10¹²) molar; Lovelock, 1971]. Since then, its atmospheric levels have grown steadily, reaching levels of 4.7 ppt in 2000 [Montzka and Fraser, 2003]. Global atmospheric SF₆ levels have been measured by satellite showing an annual growth rate (2002-2003) of 5-8% yr⁻¹ [Burgess *et al.*, 2004].

Although it is present in the background atmosphere in very low concentrations, it has been included in the Kyoto Protocol because of its large GWP and persistent growth rate [4-5% per year, Montzka and Fraser, 2003]. A more extensive global program of atmospheric SF₆ measurements has been recommended to review and verify SF₆ emission inventories provided by national governments [Harnisch and Hohne, 2002]. By 2100, SF₆ is estimated to reach 60 ppt or more in the background atmosphere [Nakicenovic, 2000].

Sulfur hexafluoride has proved invaluable as a stable tracer in studies of exchange processes between different water masses within lakes, between the atmosphere and the oceans, between air and the firn-ice system and between the troposphere and the stratosphere [Harnisch, 1999].

Sulfur hexafluoride measurements have been made on air samples from the Cape Grim air archive (collection commenced in 1978) and from stainless

steel flasks filled at Cape Grim for the University of Heidelberg [UH; Maiss *et al.*, 1996; Maiss and Brenninkmeijer, 1998; Levin *et al.*, 2003 and earlier *Baseline* reports], for the University of East Anglia [UEA; Oram, 1999], for the Scripps Institution of Oceanography [SIO; Vollmer and Weiss, 2002] and for NOAA-CMDL [Geller *et al.*, 1997; Hall *et al.*, 2002].

Based on UH atmospheric observations from Cape Grim and other background locations, global annual emissions of SF₆ were calculated to peak in 1995 at 6,700 tonnes, declining to 5,600 tonnes in 1996 and less than 5,000 tonnes in 1998 [Maiss and Brenninkmeijer, 2000]. Similar global emissions of 5,900 tonnes in 1996 have been reported [Geller *et al.*, 1997], based on observations from the NOAA-CMDL global network. Further analysis of data from the NOAA-CMDL network suggests that global emissions may have increased in 2002-2003 compared to 1998-2001 [Thompson *et al.*, 2004]. Using inter-species correlation techniques, *in situ* SF₆ and perchloroethylene (C₂Cl₄) measurements from a 500-metre tower in North Carolina, USA, have been used to estimate North American SF₆ emissions of 2400±500 tonnes in 1995 [Bakwin *et al.*, 1997], about 35% of global emissions.

Emissions are dominated by releases from electrical equipment (75%), with 7% from magnesium production, 6% from adiabatic applications (tyres and shoes), 5% from aluminium degassing, 4% from the electronics industry and 3% from insulated windows. By the mid-1990s, global sales of SF₆ had reached about 8,500 tonnes yr⁻¹, with 75% of sales in the 1990s being released to the atmosphere and 25% banked in electrical equipment and insulating

windows. Within the global electrical equipment sector (more likely to represent the use pattern of SF₆ in Australia), 32% of annual SF₆ sales is banked into equipment and 68% of sales is used to replace SF₆ that has escaped from electrical equipment [Maiss and Brenninkmeijer, 1998].

Cape Grim *in situ* measurements on the AGAGE (Advanced Global Atmospheric Gases Experiment) GC-MS-ADS [Prinn *et al.*, 2000] commenced in June 2000, with the aim being to produce a more precise record, through higher sampling frequency, compared to those obtained from the various flask records. In addition, it was planned to derive regional emissions of SF₆ from data collected when air masses reached Cape Grim after passing over regional SF₆ sources such as Melbourne and environs, an urban complex of 3.5 million people, 250 km north of Cape Grim.

Unfortunately, the AGAGE GC-MS-ADS data proved to be noisy and unreliable because of poor repeatability of trapping on the adsorption-desorption system (ADS) used. It was then decided in 2001 to initiate another *in situ* SF₆ measurement project using GC-ECD (gas chromatography with electron capture detection), a widely used and reliable technique for this species. A new instrument (GC-MS-Medusa), which can measure SF₆ with improved precision, was installed at Cape Grim in January 2004. It is planned to run this new instrument in parallel with the GC-ECD instrument for six months or more during 2004 to obtain a reliable instrument inter-comparison.

2. Instrument design and methodologies

A GC system designed to measure SF₆ was assembled and commenced measurements in late March 2001. The instrument is based on a Shimadzu model GC-14A, fitted with a ⁶³Ni 370 MBq ECD. The ECD is operated at 325°C in constant current, variable frequency mode, with the current set at 1.0 nA.

The sample loop volume is nominally 3 ml and dry air samples are injected directly to a 1 m x 3/16" O.D. stainless steel column packed with a 60-80 mesh 5A molecular sieve to separate SF₆ from air. The column oven temperature is 40°C (isothermal). The carrier gas is high purity nitrogen (BOC grade 4.0), further purified by a 5A molecular sieve trap at room temperature and a Supelco high capacity gas purifier, model #23801. Carrier gas flow-rate is 40 ml min⁻¹.

Two Valco valves with electric actuators are used, the first (EQ36 – 2 position, 3 port) selecting either ambient air from the main 10-m air intake stack via a metal bellows pump (MB-21E), or working standard air from a pressurised stainless steel tank. Both air streams are dried by passage through a cartridge type Nafion® dryer [Folger and Simmonds, 1979], and then fed to the second valve (E4C10P) which switches the sample loop between 'load' and 'inject' positions. The sample loop is flushed with the selected air stream for 30 seconds at 60 ml min⁻¹. For ambient measurements the flush pump is switched on and purged for 60 seconds prior to the loop flush.

The valves, air pump and a HP3396A integrator are controlled by a PC (Samsung 386), via its parallel port and a custom-built relay interface unit. The ECD output analogue signal is connected to the integrator, which digitises the chromatographic data. Initially the integrator was used to process the chromatograms with the resulting report files being collected by the PC via a serial communications link. Since July 2001 the PC also acquires and stores the raw data for each chromatogram from the integrator, which are later imported by the AGAGE chromatography software on a separate computer for batch integration and processing.

3. Standard gases

Dry ambient air SF₆ mole fractions are obtained by comparison to working standards. The operating sequence alternates between standard and ambient measurements. The current sequence is for a sample injection every 15 minutes, i.e. an ambient air sample every 30 minutes. In the past, the instrument has been programmed at various times for injections at intervals of 12, 13, 15 and 20 minutes.

The working standard gases used (Table 1) are supplied from an internally-electropolished 15-litre or 35-litre stainless steel tank, refilled as required at Cape Grim under baseline conditions. The working standards are calibrated against a secondary standard, J-042, a sample of compressed, natural air, contained in a 35-litre internally-electropolished stainless steel tank, filled at Trinidad Head, California [Prinn *et al.*, 2000]. A comparison of J-042 against another secondary standard, J-064, in September 2002 allowed the whole SF₆ data set to be directly referenced to the Scripps Institution of Oceanography SIO-1998 scale, using the SIO assigned concentration for J-064. J-064 was assigned an SF₆ concentration of 4.698±0.012 ppt by indirect comparison with SIO primary standards on 5 June 2002.

Table 1. Natural air secondary and working standards used in the calibration of SF₆ *in situ* measurements at Cape Grim. Mole fractions are listed in the SIO-1998 scale. Standards are wet, baseline air, cryo-trapped (-196°C) at Cape Grim into an evacuated, electropolished 15 L stainless steel tank.

Tank #	Date On	SF ₆ (ppt)
J-064		4.698
J-042		4.436
CG010319	22 Mar 2001	4.530
CG010618	01 Jul 2001	4.584
CG011108	12 Nov 2001	4.635
CG020328	03 Apr 2002	4.707
CG020620	21 Jun 2002	4.771
CG021022	22 Oct 2002	4.884
CG030117	20 Jan 2003	4.918
G-094	14 May 2003	4.837 (35 litre tank)
GR-097	26 Jun 2003	4.909 (Rix pump filled 35 litre tank)
CG300404	14 May 2004	5.203 interim; # to be relabelled
G-109	11 Aug 2004	5.310 interim

Figure 1 shows comparisons of AGAGE *in situ* SF₆ data with flask data from SIO, UH, UEA and NOAA-CMDL at Cape Grim. The average ratios of AGAGE *in situ* data to flask data are: SIO/AGAGE, 1.01 ± 0.02 (23); UH/AGAGE, 1.01 ± 0.01 (19); UEA/AGAGE, 1.04 ± 0.03 (7) and NOAA-CMDL/AGAGE, 1.01 ± 0.01 (113). The AGAGE *in situ* data agree to within 1% of SIO, UH and NOAA-CMDL flask data and to within 4% of UEA data.

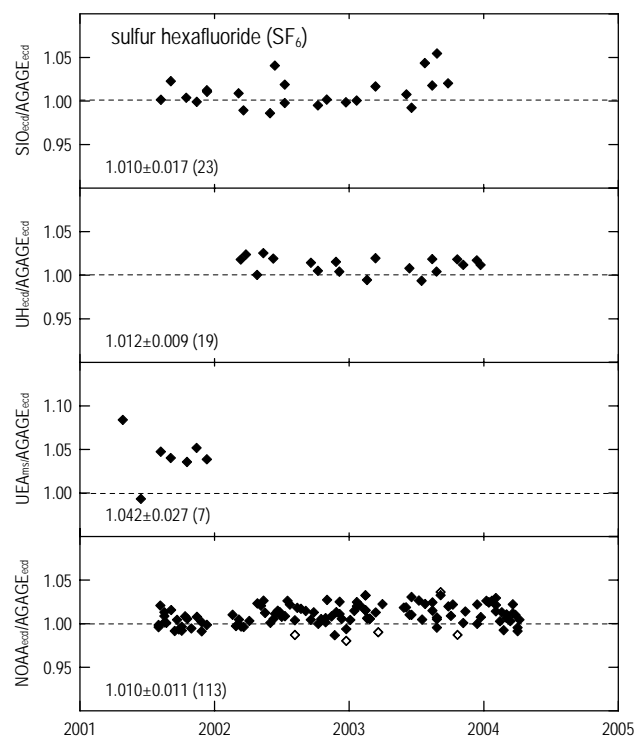


Figure 1. Comparisons of AGAGE_{ecd} *in situ* SF₆ data with flask data from SIO_{ecd}, UH_{ecd}, UEA_{ms} and NOAA-CMDL_{ecd} at Cape Grim. The subscripts indicate the respective measurement techniques employed by the different laboratories. Mean ratios shown are calculated using solid symbol data; open symbol data have been removed after applying a 2σ filter to detrended data.

The *in situ* and SIO flask data are reported in the same gravimetric calibration scale [SIO-1998; Prinn *et al.*, 2000], which is estimated to have an absolute accuracy of 2% for SF₆ [Vollmer and Weiss, 2002]. The UH data are reported in an independent calibration scale, based on a primary standard, with an estimated absolute accuracy of $\pm 1.1\%$, which was prepared by gravimetric dilution of a commercial gravimetric standard [Maiss *et al.*, 1996]. The NOAA-CMDL data are reported in an independent scale prepared by gravimetric dilution of pure SF₆ [Geller *et al.*, 1997]. The UEA data are reported in a scale based on a NOAA-CMDL standard [Oram, 1999]. NOAA-CMDL have prepared two gravimetric SF₆ calibration scales, the first called the 1994 scale [Geller *et al.*, 1997] and the second the 2000 scale, which agrees with the 1994 scale to within 2% [Hall *et al.*, 2002]. The NOAA-CMDL data reported here are in the 2000 scale. The cause of the difference (4%) between UEA (presumably reported in the NOAA-CMDL 1994 scale) and NOAA-CMDL data

reported for Cape Grim in this paper is unknown, but it is possible that some of the difference is due to changes in the NOAA-CMDL SF₆ calibration scale.

SIO and UH measurements of SF₆ at Cape Grim have been independently reported to agree to within 1% [Vollmer and Weiss, 2002]. The NOAA-CMDL 1994 and UH SF₆ calibration scales have also been reported to agree within 1% [UH/NOAA-CMDL 1994 = 1.01 ± 0.03 ; Geller *et al.*, 1997]. From the Cape Grim data above, UH/NOAA-CMDL 2000 = 1.00 ± 0.01 .

During the measurement period (2001–2003), SF₆ concentrations have grown by more than 10% (0.6 ppt), and the comparison with UH measurements over the same period shows no evidence of concentration dependent differences, suggesting that, over the concentration range measured, the respective instruments are behaving linearly. The maximum enhancements of SF₆ during pollution episodes at Cape Grim are about 5% (0.3 ppt), so the assumption of linearity in assigning concentrations during these pollution episodes should be sound.

4. Data

4.1. Identification of pollution

The identification of ‘non-baseline’ periods is carried out by AGAGE personnel at Georgia Institute of Technology (GIT), using an objective, automated algorithm [Prinn *et al.*, 2000]. The algorithm considers a 4-month period centred on each observation. After removal of a second-order polynomial fit to the data in this period, the algorithm seeks to identify a statistically normal distribution of unpolluted (baseline) mole fractions over this period. This is achieved by iteratively removing (and labelling as pollution) those mole fractions which exceed the median plus 2.5 standard deviations. Simultaneously, the algorithm fits a normal distribution to these baseline values to produce a mean and standard deviation of the distribution. Further checks, using standard synoptic analyses and back trajectory calculations, ensure that the pollution events so identified are meteorologically reasonable.

4.1.1. Baseline data

The monthly mean baseline SF₆ data (pollution episodes removed) for 2001–2003 are presented in Table 2. Figure 2 shows all (baseline monthly means and non-baseline) instrumentally valid data. Data were not obtained for two extended periods: 24 December 2001 to 5 February 2002, due to loss of the integrator program after a lightning strike, and 14 April to 23 May 2003 due to a variety of instrumental problems. The average annual growth rates in SF₆ observed at Cape Grim from the AGAGE program over the period 2001 to 2003 are listed in Table 2. The growth rates are calculated using the curve fitting techniques of Thoning *et al.* [1989], by finding a long-term trend curve with 650-day smoothing and seasonal cycles removed. The derivative of the long-term trend curve is then taken to give an instantaneous growth rate curve. The annual average growth rates are then produced from such curves.

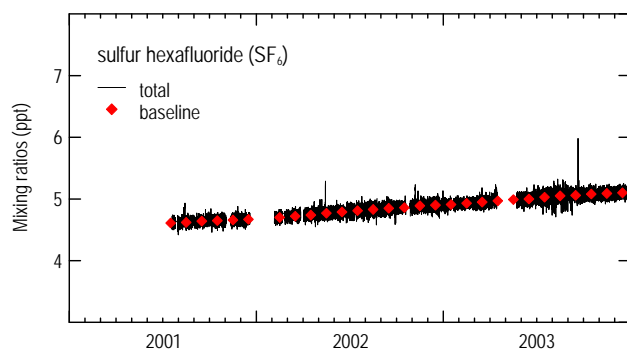


Figure 2. Total (black) and baseline monthly mean (♦) *in situ* observations of SF₆ (ppt) made at Cape Grim on the Shimadzu gas chromatograph over the period July 2001 to December 2003.

Table 2. Cape Grim baseline monthly mean SF₆ dry air mole fraction (ppt) reported in the SIO-1998 scale. Annual means are obtained from monthly means, monthly means from individual measurements. Data updated by GIT, July 2004.

Month	2001		2002		2003	
	SF ₆ (ppt)	sd (ppt)	SF ₆ (ppt)	sd (ppt)	SF ₆ (ppt)	sd (ppt)
Jan					4.91	0.04
Feb			4.70	0.04	4.93	0.04
Mar			4.72	0.04	4.95	0.04
Apr			4.74	0.05	4.97	0.06
May			4.77	0.05	4.99	0.05
Jun			4.79	0.05	5.00	0.05
Jul	4.61	0.05	4.81	0.05	5.03	0.06
Aug	4.62	0.04	4.83	0.05	5.05	0.07
Sep	4.64	0.05	4.85	0.05	5.06	0.06
Oct	4.65	0.04	4.86	0.04	5.08	0.05
Nov	4.66	0.04	4.89	0.04	5.09	0.05
Dec	4.67	0.04	4.90	0.05	5.10	0.05
Annual	4.64	0.02	4.81	0.07	5.01	0.06
Growth rate (ppt yr ⁻¹)	0.211	0.007	0.223	0.039	0.191	0.049
(% yr ⁻¹)	4.550	0.174	4.647	0.746	3.819	1.000

The annual average SF₆ baseline mixing ratios in 2002 and 2003 were 4.81 and 5.01 ppt respectively. The 2002 and 2003 growth rates were 0.22 and 0.19 ppt yr⁻¹ respectively.

Figure 3 shows Cape Grim baseline monthly mean *in situ* and flask (SIO, UH, UEA, NOAA-CMDL) data (1978-2003). The data are reported in their individual SF₆ calibration scales. Small differences between the various laboratories can be seen in the data from the mid 1990s onwards, as shown in Figure 1. However, these differences are not maintained consistently throughout the complete record. UEA data are lower than UH during the 1970s and 1980s whereas the UEA data are higher than UH since the early 1990s. This indicates possible non-linearities in either or both records [Oram, 1999]. The UH GC-ECD instrument is reported to be linear over a 200-fold range of SF₆ concentrations [Maiss *et al.*, 1996].

Figure 4 shows the Cape Grim baseline monthly mean *in situ* and flask (UH) data (1978-2003) and the long-term growth rate. The UH data were chosen for this analysis because of their long record at Cape Grim (1978-2003) and the well-behaved intercomparison with AGAGE *in situ* data (Figure 1). The growth rate data were calculated from both *in situ* and flask data,

with the flask data adjusted to best-fit the *in situ* data to allow for possible differences due to calibration scales, sample storage and analytical procedures.

The growth rate of SF₆ increased steadily in the Cape Grim record from 0.1 ppt yr⁻¹ in the late 1970s (16% yr⁻¹) to 0.24 ppt yr⁻¹ in mid-1990s (4% yr⁻¹). Since 1995 the growth rate has not increased, varying between 0.21 and 0.24 ppt yr⁻¹ (5-8% yr⁻¹), suggesting that global emissions have remained relatively constant since 1995.

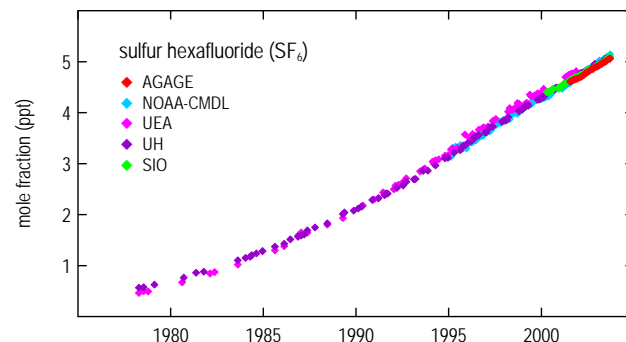


Figure 3. Cape Grim monthly mean *in situ* (AGAGE) and flask (archive: UEA, UH; ambient: SIO, NOAA-CMDL, UEA, UH) SF₆ data.

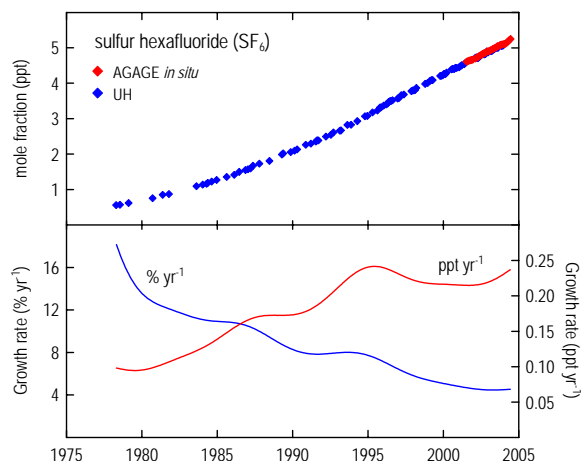


Figure 4. Cape Grim monthly mean *in situ* (AGAGE) and flask (UH, archive and ambient) SF₆ data; trends (% yr⁻¹, ppt yr⁻¹) are calculated on *in situ* and flask (adjusted to best-fit *in situ*) data.

4.1.2. Non-baseline data

A feature of the SF₆ data is the occasional occurrence of pollution episodes (Figure 2). These are found in air masses at Cape Grim that have previously passed over the Port Phillip region, including the major urban complex, Melbourne, and the major regional city, Geelong. Eleven significant SF₆ pollution events originating from the Port Phillip region have so far been identified at Cape Grim in 2001 (11 August), 2002 (23-24 April, 4, 8, 15 May, 15 September, 7 November) and 2003 (12, 17 March, 20, 22 September). The 7 November event of 2002 is shown in Figure 5. During this pollution episode, SF₆ levels were elevated by up to 7% (0.3-0.4 ppt), CO levels by up to 200% (120 ppb - parts per billion (10⁹) molar) and HFC-134a (for comparison) by up to 90% (18 ppt).

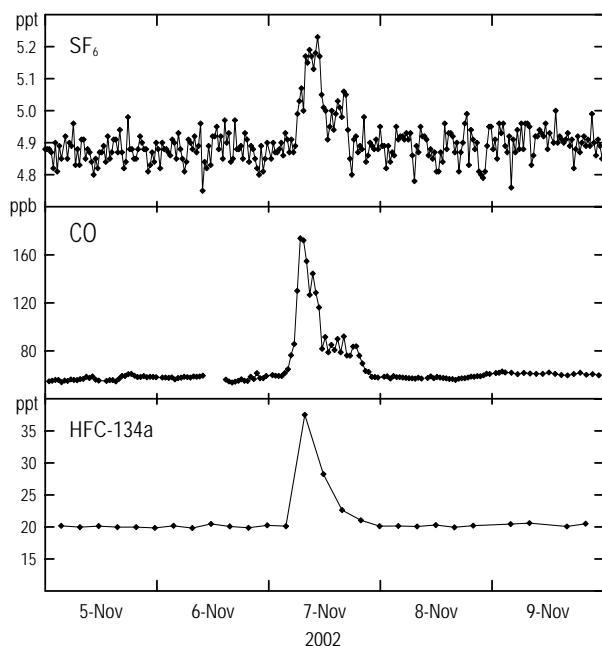


Figure 5. Port Phillip region pollution events for SF₆, HFC-134a and CO observed at Cape Grim on 7 November 2002.

The process of estimating SF₆ emissions involved first identifying pollution episodes in the Cape Grim record that were attributed to air masses that passed over the Port Phillip region before travelling across Bass Strait to Cape Grim. Pollution markers (CFC-12, CH₂Cl₂ and HFC-134a) were used to identify episodes caused by Port Phillip emissions. These ‘pollution episodes’ were extracted, and correlations between the trace species in the polluted air masses were derived. Linear regressions applied to the data were performed using a Reduced Major Axis (RMA) regression procedure [Davis, 1986]. These correlations and an estimate of CO emissions from Port Phillip were used to deduce the mass of Port Phillip emissions.

Figure 6 shows back-trajectories for the eleven pollution episodes, indicating that the air passed over or near Melbourne some 6–12 hours before arriving at Cape Grim. Figure 7 shows the elevation in SF₆ levels compared to CO levels for the eleven identified SF₆ pollution episodes at Cape Grim.

Emissions of SF₆ (3.0 ± 1.5 tonnes yr⁻¹) from the Port Phillip region were deduced from these episodes during 2001–2003, assuming CO emissions from this region of 680,000 tonnes yr⁻¹ [EPA, 1998; NPI, 2003], which include an assumed 25% uncertainty in CO emissions. This is the first measurement-based estimate of regional SF₆ emissions in Australia. The Port Phillip region contains $20 \pm 1\%$ of Australia’s population [EPA, 1998] and, assuming SF₆ emissions are proportional to population, leads to an estimate of Australian SF₆ emissions during 2001–2003 of 15 ± 7.5 tonnes yr⁻¹, or 0.75 tonnes per million people. In GWP terms the SF₆ emissions are equivalent to 0.18–0.54 M tonnes of CO₂ [$< 0.1\%$ of Australia’s total greenhouse gas emissions in 2000; AGO, 2002].

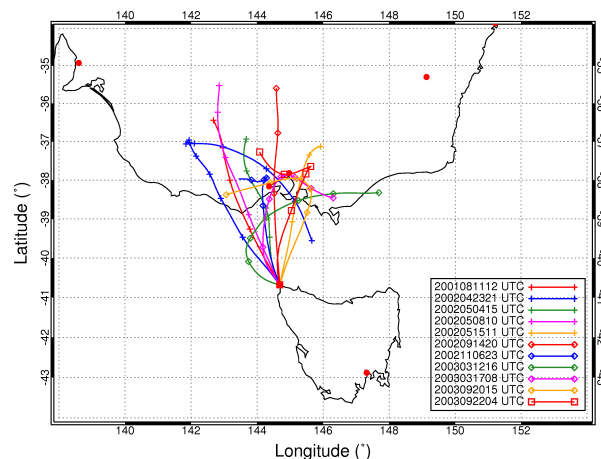


Figure 6. HYSPLIT [Draxler and Rolph, 2003] back-trajectories for the 11 identified SF₆ pollution episodes at Cape Grim. All the trajectories were run with an endpoint height at Cape Grim of 100 m.

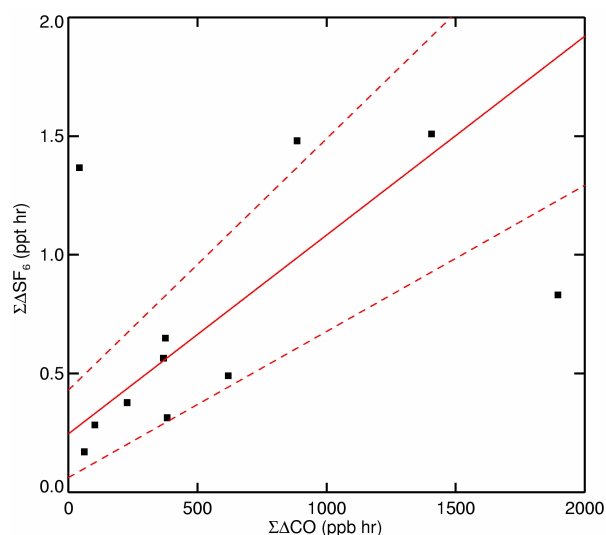


Figure 7. The elevation in SF₆ levels compared to CO levels for the 11 identified SF₆ pollution episodes at Cape Grim. The best-fit slope (SF₆-ppt/CO-ppb) is 0.00084 ± 0.00022 .

The only SF₆ emissions listed currently in the Australian National Greenhouse Gas Inventory (NGGI) are 0.1 tonnes in 2000 from metal production [AGO, 2002]. Australian SF₆ emissions from the electricity transmission and distribution sector have been estimated to be as high as 75 tonnes in 1996/1997, based on US SF₆ emission factors (4.1 tonnes of SF₆ per million people) [AGO, 2000], but these estimates have not yet been included in the NGGI. Since 1996/1997 US SF₆ emission factors for this sector have declined by a factor of 2 [2.1 tonnes per million people in 2002, US EPA 2004]. Applying the latter emission factor to Australia would imply Australian emissions from this sector of about 40 tonnes yr⁻¹ in 2002. The UK, New Zealand and the EU have reported SF₆ emissions factors for the electricity transmission and distribution sector of 0.2, 0.4 and 0.7 tonnes per million people respectively [AGO, 2000; NZGGI 2000], significantly lower than the US factors. The possible reasons for these differences between nations are not obvious.

5. Conclusions

Long-term observations of SF₆ at Cape Grim have shown a growth rate that increased from 0.1 ppt yr⁻¹ in the late 1970s to 0.24 ppt yr⁻¹ in the mid-1990s. Since then, the SF₆ growth rate has remained relatively constant at 0.23 ± 0.02 ppt yr⁻¹. These data suggest that global emissions of SF₆ have been relatively constant (±10%) over the past 5 years.

An analysis of SF₆ pollution episodes at Cape Grim suggests that SF₆ emissions in the Port Phillip region were 3±1.5 tonnes yr⁻¹ during 2001-2003, which have been extrapolated to estimate Australian emissions of 15±7.5 tonnes yr⁻¹, indicating an overall SF₆ emission factor for Australia of 0.75 tonnes per million people. This emission factor is near the middle of the range reported by the US, UK, EU and NZ (0.2 to 2.1 tonnes of SF₆ per million people).

Continued monitoring of SF₆ at Cape Grim, using a higher precision instrument (AGAGE GC-MS-Medusa), which was installed in early 2004, should lead to more accurate estimates of regional SF₆ emissions.

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<http://www.arl.noaa.gov/ready.html>

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